Pesticide Transport with Runoff from Turf: Observations Compared with TurfPQ Model Simulations

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Pesticides applied to turf grass have been detected in surface waters raising concerns of their effect on water quality and interest in their source, hydrological transport and use of models to predict transport. TurfPQ, a pesticide runoff model for turf grass, predicts pesticide transport but has not been rigorously validated for larger storms. The objective of this study was to determine TurfPQ's ability to accurately predict the transport of pesticides with runoff following more intense precipitation. The study was conducted with creeping bentgrass [*Agrostis palustris* Huds.] turf managed as a golf course fairway. A pesticide mixture containing dicamba, 2,4-D, MCPP, flutolanil, and chlorpyrifos was applied to six adjacent 24.4 by 6.1 m plots. Controlled rainfall simulations were conducted using a rainfall simulator designed to deliver water droplets similar to natural rain. Runoff flow rates and volume were measured and water samples were collected for analysis of pesticide concentrations. Six simulations yielded 13 events with which to test TurfPQ. Measured mean percentage of applied pesticide recovered in the runoff for dicamba, 2,4-D, MCPP, flutolanil, and chlorpyrifos was 24.6, 20.7, 14.9, 5.9, and 0.8%, respectively. The predicted mean values produced by TurfPQ were 13.7, 15.6, 15.5, 2.5, and 0.2%, respectively. The model produced correlations of $r = 0.56$ and 0.64 for curve number hydrology and measured hydrology, respectively. Comparisons of the model estimates with our field observations indicate that TurfPQ under predicted pesticide runoff during 69.5 ± 11.4 mm, 1.9 ± 0.2 h, simulated storms.

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Turf grass represents the largest single crop grown in the United States. According to one estimate, more than 16 million hectares of U.S. land are covered by tended lawn (Milesi et al., 2005). Turf is seeded on private and public property for both aesthetic and utilitarian purposes; residential lawns, city parks, cemeteries, and athletic fields commonly employ turf for land coverage. Maintaining the health and beauty of turf often requires chemical fertilization, thatch treatments, and pesticide application. Application rates for turf are considerably higher than those used for agriculture (Barbash and Resek, 1996; Gianessi and Anderson, 1996). The highest intensity management practices are performed for golf courses (Smith and Bridges, 1996). The substantial amount of chemical applications used at golf courses have raised concerns in recent years, particularly regarding the potential for contamination in runoff waters produced by flash flooding or storm events. According to recent water quality studies, pesticides that are commonly applied to turf grasses have been found in water samples close to urban areas (Cohen et al., 1999; Gilliom et al., 2006). These findings have motivated the study of turfgrass hydrology and chemical transport as well as hydrological transport modeling. The ability to predict future outcomes using computer models is a valuable tool for ecological and human risk assessment.

For the most part, chemical transport modeling of turf has been performed using existing agricultural or watershed models such as GLEAMS (Smith and Tillotson, 1993; Ma et al., 1999a), EPIC (King and Balogh, 1997; King and Balogh, 1999), PRZM (Cohen et al., 1993; Ma et al., 1999a; Durborow et al., 2000), SWAT (King and Balogh, 2001), Opus (Ma et al., 1999b), EXPRES (Roy et al., 2001), and RZWQM (Schwartz and Shuman 2005). To our knowledge the only model developed specifically for turf grass is TurfPQ (Haith, 2001; Haith, 2002). Although this model has been used for theoretical risk assessment studies (Haith and Rossi, 2003; Vincelli, 2004; Haith and Duffany, 2007), it has not been rigorously tested with numerous data sets. The focus of this study was to compare measured

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Abbreviations: 2,4-D, dimethylamine salt of 2,4-dichlorophenoxyacetic acid; CN, curve number; HPLC, high performance liquid chromatography; K_{OC}, organic carbon partition coefficient; MCPP, Mecoprop-p; NRCS, Natural Resources Conservation Service; OC, organic carbon; OFW, organic-free water; TurfPQ_CN, TurfPQ results with curve number hydrology; TurfPQ_MH, TurfPQ results with measured hydrology.

pesticide mass loss data in runoff water from fairway turf to model estimates generated with TurfPQ. Data was collected from a 3-yr plot study measuring the transport of three herbicides (dicamba, 2,4-D, and MCPP), one fungicide (flutolanil), and one insecticide (chlorpyrifos) in runoff from turf. These pesticides were selected based on their range in physical properties (Table 1) and common use in turf management. Model predictions were compared to actual results for these compounds.

Materials and Methods

Site Description

Runoff data was collected from turf plots located at the University of Minnesota Turf Research, Outreach and Education Center, Saint Paul, MN. The 976 m^2 site contained a natural slope running east to west that was graded to 4% with <1% slope from north to south. The soil consisted of Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludolls) with 3% organic carbon, 29% sand, 55% silt, and 16% clay. Creeping bentgrass sod (L-93) was planted 14 mo before initiation of the runoff studies and managed as a fairway with 1.25 cm height of cut (three times weekly) and weekly sand top dressing (1.6 mm).

The site was divided into six plots (24.4 by 6.1 m, length × width). A runoff collection system similar to Cole et al. (1997) was constructed at the western edge of each plot. Stainless steel flashing at the base of each plot guided runoff from the turf into 6.1-m gutters constructed of 15.2-cm schedule 40 polyvinyl chloride (PVC) pipe cut in half length-wise. The central point of the gutter system lead to a stainless steel LG 60° V trapezoidal flume (Plasti-Fab, Tualatin, OR) equipped with a bubble-tube port and two sample collection ports. The gutter system and trapezoidal flume were embedded in sand-filled trenches, solidifying the gutter at a ≤ 2% slope on each side and maintaining the flume at a horizontal level condition. This design promoted the flow of water to the flume, while allowing the effects of friction to be negated in the gutter so that accurate flow rate and runoff volume could be attained. Gutter covers and flume shields prevented outside precipitation from entering the collection apparatus. Plots were hydrologically isolated from each other with removable berms consisting of inverted horizontally-split 10.2-cm schedule 40 PVC pipe. Observation of water flow during runoff events showed no water movement under the PVC berms.

Turf management practices were evaluated during the three field seasons, with half of the plots receiving hollow tine aerification (0.95 cm internal diam. × 11.43 cm length) and the remaining plots receiving other management practices. Plots aerated with hollow tines were managed identically for the three field seasons. Data used in this manuscript are limited to plots managed with hollow tine aerification (plots 2, 4, and 5 for simulations number 1 and 2 in 2005, 2006, and 2007; plots 1 and 6 for simulation number 1 in 2006).

Pesticides

Pesticides monitored in the experiment were as follows: Dursban 50W insecticide (Dow AgroSciences LLC, Indianapolis, IN) containing 50% chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate); ProStar 70WP fungicide (Chipco Professional Products, Bayer CropScience, Research Triangle Park, NC) containing 70% flutolanil (N-[3-(1-methylethoxy) phenyl]-2-(trifluoromethyl) benzamide); and Trimec Bentgrass Formula herbicide (PBI Gordon, Kansas City, MO) containing 9.92% Mecoprop-p (dimethylamine salt of (+)-(*R*)-2-(2-methyl-4-chlorophenoxy) propionic acid), 6.12% 2,4-D (dimethylamine salt of 2,4-dichlorophenoxyacetic acid), and 2.53% dicamba (dimethylamine salt of 3,6-dichloro-o-anisic acid). These commercially available products were tank-mixed and applied, at recommended rates, to all plots perpendicular to runoff flow. Glass Petri dishes (14-cm diam.) were distributed throughout the plots before application to allow for verification of application rates. The mean application rate of each pesticide is given in Table 1.

Simulated Precipitation

Approximately 50 h before each simulation, the turf was prewet beyond saturation (volumetric water content: 68 ± 3%) using maintenance irrigation. This ensured uniform moisture distribution and allowed background samples to be collected. The following day the turf was mowed (1.25 cm height, clippings removed) and runoff collection gutters and flumes were cleaned. Pesticides were applied and simulated precipitation was initiated 8 to 36 h following application once wind speeds dropped and remained below 2.2 m s^{-1} (Davis Instruments, Hayward, CA). Volumetric soil moistures measured approximately 2 h before initiation of precipitation were 45 ± 4%.

Simulated rainfall was applied using an overhead irrigation system described in U.S. patent 5279,151 (Coody and Lawrence, 1994). This apparatus is designed to produce the droplet size spectrum, impact velocity, and spatial uniformity characteristic of natural rainfall. The simulator in this study consisted of 5-cm schedule 40 PVC pipe used for the base, which guided water flow to 18 2.54-cm schedule 40 PVC risers each fitted with a pressure regulator (Lo-Flo, 15 psi) and a nozzle (no. 25) containing a standard PC-S3000 spinner (Nelson Irrigation, Walla Walla, WA). Risers were spaced 3.7 m apart with nozzles and spinners suspended 2.7 m above the turf. To attain the required water pressure, the rainfall simulator could only be engaged on two plots at a time (20 ± 8 h following pesticide application). Due to slight variations in wind speed and water pressure for each paired experiment, the rainfall simulator had the potential to deliver slightly different amounts of precipitation to each plot. Therefore, unlike the pesticide application rate which was averaged over all six plots per simulation, the total rainfall was measured on a plot-by-plot basis. Precipitation was measured using 12-cm rain gauges (Taylor Precision Products, Oak Brook, IL). A total of 12 rain gauges were placed in the same grid pattern over each plot. The two highest and two lowest readings were rejected and the total rainfall was computed as the mean of the remaining eight measurements. Each plot was treated as a separate experiment with a unique amount of rainfall for the purposes of modeling. Rainfall simulations were conducted twice per year during the growing season. Dates and designations are as follows: 22 Aug. 2005 (2005–1), 29 Sept. 2005 (2005–2), 15 Aug. 2006 (2006–1), 4 Oct. 2006 (2006–2), 7 Aug. 2007 (2007–

1), and 25 Sept. 2007 (2007–2). Precipitation rates were 36.2 ± 5.9 mm h^{-1}; similar to storm intensities recorded in Minnesota during July through October. The duration of the simulated precipitation was 1.9 ± 0.2 h, which was chosen to assure 90 min of runoff had been generated from each plot. The average precipitation rate and duration of our simulated rainfall events represent a 2 h storm duration with recurrence interval of 25 yr (Huff and Angel, 1992).

Runoff Collection and Analysis

For each plot, runoff flow was measured with an automated flow meter (Isco model 730, Lincoln, NE) connected near the base of the flume. Water samples were collected from the flume at the initiation of runoff and at 5-min intervals after the first runoff using an automated sampler (ISCO model 6700, Lincoln, NE) containing 24, 350-mL glass bottles. Samples were stored frozen (–20°C) until analysis. Each sample was analyzed for pesticides. No samples were combined.

Runoff samples were prepared for high performance liquid chromatography (HPLC) analysis by passing 3 mL of sample through a 0.45 μm nylon syringe filter (Whatman Inc, Clifton, NJ) followed by 0.5 mL of methanol to rinse the filter. For application verification analysis, Petri dish samples were rinsed six times with methanol, filtered (0.45 μm nylon filter), then diluted with a 6:1 ratio of laboratory-grade organic-free water (OFW)/methanol to maintain a similar water/methanol ratio of the filtered runoff samples. All samples prepared for HPLC analysis were filtered in batches of 10, followed by two control samples, a pure OFW sample and an OFW spike which contained the five target analytes. Quantitative analysis of chlorpyrifos, dicamba, flutolanil, MCPP, and 2,4-D were measured by direct injection of 500 μL of the filtered sample onto a high performance liquid chromatograph (HPLC, Waters model 717 plus autosampler and model 1525 binary pump) with a photodiode array detector (DAD, Waters model 2996: Waters, Milford, MA) monitoring at 230 nm. Two solvents [solvent A: laboratory-grade organic-free water (0.17% trifluoroacetic acid); solvent B: 82:18 methanol/acetonitrile] eluted analytes from a 150 mm long, 4.6 mm diam. C-18 column with 5 μm packing (Agilent, New Castle, DE) at a rate of 1 mL min^{-1} with the flow program as follows: initial conditions, 60% B, were held for 2 min followed by a gradient ramped from 60 to 95% B in 23 min, a 3 min hold, then back to 60% B in 10 min with a 5 min hold. Method detection limits ranged from 2.5 to 3.7 μg L^{-1}. Limits of quantification for the target analytes were: chlorpyrifos 5.3 ± 0.9 μg L^{-1}, dicamba 5.1 ± 0.6 μg L^{-1}, flutolanil 4.5 ± 0.8 μg L^{-1}, MCPP 5.3 ± 0.9 μg L^{-1} and 2,4-D 4.5 ± 0.8 μg L^{-1}. Recoveries were: chlorpyrifos 74 ± 23%, dicamba 102 ± 6%, flutolanil 91 ± 8%, Mecoprop-p 104 ± 7% and 2,4-D 105 ± 11%. Analysis of the source water applied as maintenance irrigation and simulated precipitation contained no residues of the chemicals of interest.

Runoff mass loss was calculated using the concentration and flow rate at each minute of the simulation, summed over the time period of the sample collection (bottles 1–24). Flow data was recorded every minute during the event, while the concentration data was collected at 5-min sampling intervals; concentration data between bottles was computed as the average of the two bottles spanning the data point.

Table 1. Pesticide application rate and select properties.

Pesticide	Application rate	K_{oc}†	Half life
	g ha^{-1}	L kg^{-1}	d
Dicamba‡	237.4	13	18
2,4-D‡	95.8	48	5.5
MCPP§	176.0	20	21
Flutolanil¶	3853.2	800	116
Chlorpyrifos‡	427.5	9930	30.5

† Soil organic carbon partition coefficient.
‡ USDA-ARS (2000).
§ Oregon State University (1994).
¶ Natural Resources Conservation Service (2006).

TurfPQ Model Description

A complete description of the TurfPQ model and all equations may be found in other sources (Haith, 2001, 2002). However, a brief summary will be provided in this section. The first component of TurfPQ is the estimation of runoff volume based on the Natural Resources Conservation Service (NRCS) Curve Number (CN) method as described in Haith and Andre (2000). Based on the appropriate CN, a calculation is made where total daily rainfall is divided into two categories: infiltrate or runoff (the latter will only occur if a threshold of rain is met). A second component of the model pertains to chemical fate and transport. The pesticide may exist in two main compartments, either dissolved in water or adsorbed to turf vegetation and soil. Infiltration is the first process. In this step, the dissolved pesticide is assumed to have leached into the soil and is unavailable for runoff. After the infiltration step, the runoff equilibrium is computed using the pesticide soil organic carbon partition coefficient (K_{OC}) and the organic carbon (OC) content of the turf vegetation. First-order decay is assumed, using the soil half-life of the pesticide. TurfPQ computes runoff and pesticide mass loss on a daily basis, but summarizes the totals into monthly outputs.

Implementation of TurfPQ

Of the data collected throughout the 3-yr study, some experiments were not used due to aberrant flow readings or equipment problems. From the remaining experiments, 13 were selected for comparison with TurfPQ. This selection was made so that hydrology from different types of management practices (ie, solid tine data mixed with hollow tine data) was not a confounding issue in the results of TurfPQ.

TurfPQ model and a user manual were provided by Douglass Haith (email correspondence). The program code is written in Fortran 90 and can be executed in a Windows environment. TurfPQ requires inputs of daily precipitation and temperature, CN, pesticide application rate, dates of application, K_{OC}, half-life, and OC of the turf vegetation. This information is compiled into two separated text files, a weather data file and a pesticide data file, which TurfPQ retrieves when calculating outputs.

The weather data files included temperatures recorded at a University of Minnesota St. Paul Weather station located near (~0.4 km) the turf plots. Rainfall rates were entered that matched the simulated precipitation delivered to each plot. To model a saturated field, 11.0 mm of rain was assumed to occur on each of the previous 5 d before the simulation. Rain gauge averages (n = 8) as described earlier were used for the total rainfall.

For the TurfPQ pesticide data files, literature values were used for pesticide K_{OC}, pesticide half-life, and turf OC. Values for K_{OC} and half-life are listed in Table 1. Estimation of OC based on turf height and thatch thickness is provided in Haith (2001): where our mean thatch thickness of 31.7 mm (± 6.7 mm standard deviation) for 184 core samples collected over the 3-yr study (2005–2007) produced an OC content of 37,767 kg ha^{-1}. This represents a very high OC content due to a considerably thick thatch layer observed for our plots. TurfPQ was tested for OC = 37,767 kg ha^{-1} as well as OC = 10,235 kg ha^{-1} as used by Haith (2001) for fairway turf. The latter value represents approximately 7 mm of thatch for a 12.5 mm mow height.

For this assessment two types of results were calculated with the TurfPQ model, pesticide mass loss using the hydrology based on curve number (original TurfPQ), as well as for hydrology based on measured runoff volumes. The latter calculation was performed in Microsoft Excel, using TurfPQ Eq. 11 and 13 from Haith (2001). Verifications were made that outputs from Excel equations matched those of TurfPQ. The two types of results will be referred to as TurfPQ_CN (denoting curve number hydrology), and TurfPQ_MH (denoting measured hydrology).

Results and Discussion

Prediction of Runoff Hydrology using Curve Number Method

In TurfPQ, rainfall is partitioned into infiltrate or runoff using the NRCS CN. This is a simple and widely used method for estimating runoff; however, one of the drawbacks is that rainfall intensity is not considered in the computation. In this study, CN was calibrated based on the mean percentage of runoff from total rainfall for all experiments. For the 13 experiments, the mean ± one standard deviation for the simulated rainfall was 69.5 ± 11.4 mm. The mean percent runoff for these experiments was 31.8%. For calibration, the CN was adjusted so that the mean percentage of runoff was closest to the mean measured. A CN of 57 was the best match for the data, producing a mean of 31.7% runoff for the 13 experiments. The medians of measured vs. predicted were also best for CN = 57. This is very close to the CN of 61 proposed by Haith and Andre (2000) for fairway turf on soil type B, characteristic of our plots. Figure 1 shows the measured and predicted runoff as a percentage of total rainfall when a CN of 57 was used for prediction. The standard deviation of the measured runoff is 5.8%, which we used to represent natural variability in the experiment. When considering the difference between measured and predicted runoff values, nine predictions were within one standard deviation (i.e., |measured – predicted| < 5.8), three of the predictions were within two standard deviations, and only one was outside two standard deviations. Therefore, the CN method proved to be fairly successful for predicting runoff, given the variability in the measured values.

TurfPQ Results

Results will be presented for the three different pesticide losses: measured mass loss based on Isco flow data combined with HPLC concentration data (Measured), predicted mass loss based on curve number hydrology (TurfPQ_CN), and predicted mass loss based on measured hydrology (TurfPQ_MH). Results are presented for CN = 57 and the K_{OC} and half-life values in Table 1. Total rainfall, weather data, and application rates were entered on a plot-by-plot basis, treating each plot as an individual runoff event. As mentioned in the experimental section, two values for OC were used, one representing thick thatch (37,767 kg ha^{-1}) as well as moderate thatch (10,235 kg ha^{-1}). Results are reported for OC = 10,235; this value produced better results and seemed to be a more realistic estimation of OC.

Results for Pesticides with High Mobilities

Three of the five pesticides in this study, dicamba, 2,4-D, and MCPP are considered highly mobile (K_{OC} < 150 L kg^{-1}, Swann et al., 1983) based on their K_{OC} values (Table 1). Figure 2A shows the results of dicamba for the measured, TurfPQ_CN, and TurfPQ_MH mass loss as a percentage of the applied pesticide. The figure shows that in many instances the measured values were much higher than those predicted by the model. The mean measured value for dicamba is 24.6% and the mean predicted is 13.7% for TurfPQ_CN and 13.8% for TurfPQ_MH. Figure 2B shows the results of 2,4-D and Fig. 2C the results of MCPP for mass loss as a percentage of applied pesticide. Averaging all values, 2,4-D had a mean measured mass loss of 20.7% and a mean prediction of 15.6% for TurfPQ_CN as well as TurfPQ_MH. MCPP had a mean measured mass loss of 14.9% and mean predictions of 15.5% (TurfPQ_CN) and 15.7% (TurfPQ_MH). Predictions of these two pesticides were more accurate than those of dicamba (10.9% difference). Based on the means, 2,4-D was slightly under predicted (5.1% difference) while MCPP was very close to measured (< 1% difference).

Results for Pesticides with Low Mobilities

Based on their K_{OC} values, flutolanil (K_{OC} = 800 L kg^{-1}) is considered to have a low mobility (K_{OC} = 500–2000 L kg^{-1}) and chlorpyrifos (K_{OC} = 9930 L kg^{-1}) is considered to be immobile (K_{OC} > 5000 L kg^{-1}) (Swann et al., 1983). Therefore lower percent mass loss would be expected and was observed (Fig. 2D and E). For flutolanil, the mean measured mass loss was 5.9% of application while the mean predicted mass loss was 2.5% (3.4% difference) for both TurfPQ_CN and TurfPQ_MH. For chlorpyrifos, the mean measured mass loss was 0.8% while the mean predicted mass loss was 0.2% (0.6% difference) for both TurfPQ_CN and TurfPQ_MH.

Sources of Error

Assuming that the measured values were analyzed with accuracy, the sources of error in the predictions can be separated into two main categories: errors in parameter estimation and errors in model assumptions. These will be discussed in each of the following paragraphs.

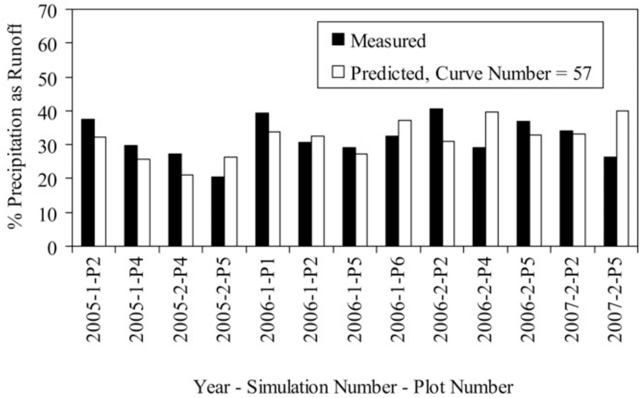

Fig. 1. Measured and predicted (TurfPQ) runoff from creeping bentgrass turf managed as a golf course fairway. Runoff quantities are reported as a percentage of total simulated precipitation.

The most likely sources of error in parameter estimation are the K_{OC} and OC values. The soil K_{OC} values that are used in the model may be an inadequate substitute for turf vegetation K_{OC} values. Additionally, the estimated OC content based on Haith (2001) could be inaccurate as these approximations were the result of a relatively small number of samples. Pesticide degradation is not a likely source of error in this experiment because the time between application and runoff (20 ± 8 h) was much less than the half-life of the pesticides evaluated (Table 1). These three sources of error are addressed in the sensitivity analysis of the following section. Curve number estimation of runoff can be eliminated as a source of error by only considering TurfPQ_MH results. Figure 2A-E indicates that CN error did not have a great impact on the prediction error as there was negligible difference (< 0.2%) between the means of TurfPQ_CN and TurfPQ_MH. Application rate and rainfall were assumed to be measured with great enough accuracy to preclude them as major sources of prediction error. Errors in application rate (based on the variation among Petri dishes) were varied in the model and found to have a negligible effect on results.

The second source of prediction error stems from the algorithms in the model itself. One assumption in TurfPQ is that infiltration is chronologically separate from runoff. In reality there is some overlap between the two processes; runoff begins while infiltration is still occurring, then gradually becomes more dominant. Although the effects may be minor, treating infiltration separately in the model can cause under predictions because more pesticide is assumed to be leached and unavailable for transport with runoff. This is most evident with larger more intense storms. TurfPQ allows for precipitation inputs at 24 h intervals while our rainfall simulator delivered the precipitation in 1.9 ± 0.2 h. The greater rainfall intensity for the measured precipitation would result in runoff before the completion of infiltration, which is in contrast to the model's assumption. Generation of runoff before completion

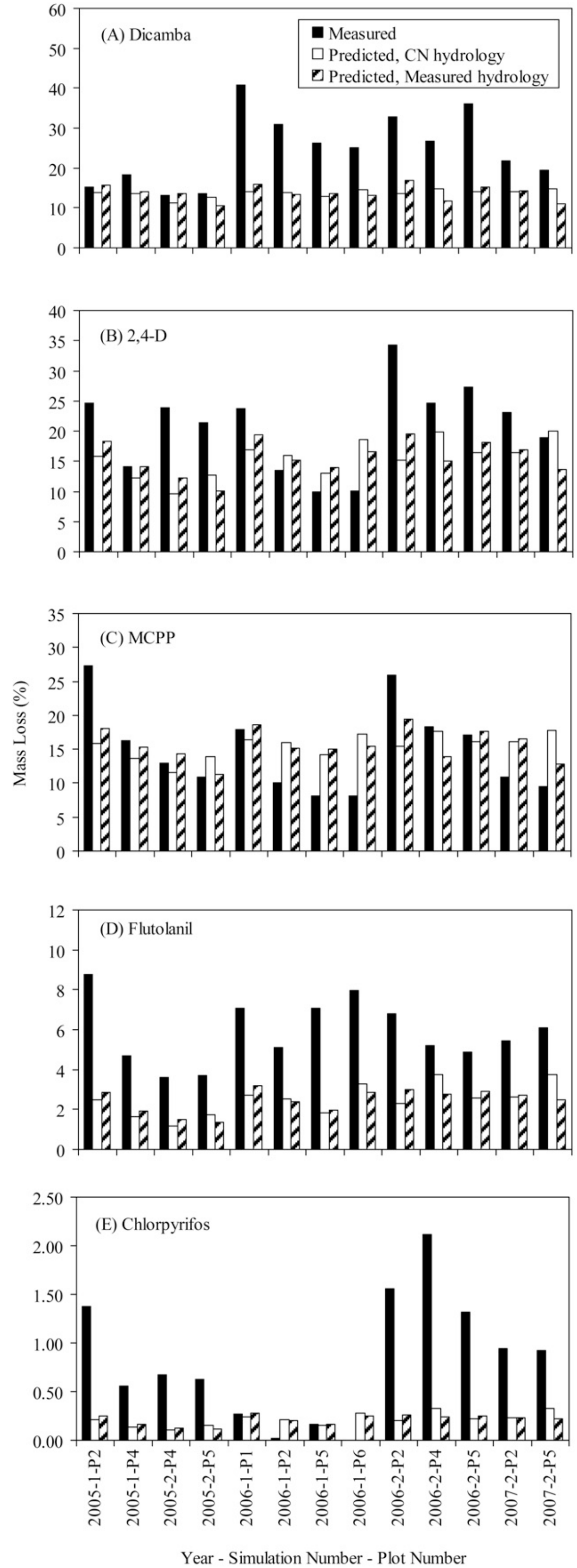

Fig. 2. (right) Measured and predicted (TurfPQ) pesticide transport with runoff from creeping bentgrass turf managed as a golf course fairway. Pesticide mass loss in runoff is reported as a percentage of applied active ingredients. Active ingredients included: (A) dicamba, (B) 2,4-D, (C) MCPP or Mecoprop-p, (D) flutolanil, and (E) chlorpyrifos. Note the difference in scale for the *y* axis from plots A through E.

of infiltration would result in greater availability of pesticides for transport in runoff. This can be illustrated with our measured data depicted in the hydrograph and chemographs in Fig. 3. Quantification of applied precipitation (69.5 ± 11.4 mm) and collection of runoff (22.2 ± 5.1 mm) for the 13 events revealed 32% of the applied water resulted as runoff. Initiation of simulated precipitation and completion of runoff collection occurred between sunset and sunrise when wind speeds were minimal and temperatures were cooler. As a result, we estimate no more than 5% of the applied precipitation would account for drift or evaporation, leaving 63% or 43.5 mm of water for infiltration. With our measured precipitation rate (0.6 ± 0.1 mm min^{-1}) it would take 72 min to generate 43.5 mm of water. Therefore according to the model's assumption infiltration would occur from 0 to 72 min and runoff would begin after its completion. However, looking at the hydrograph and chemographs (Fig. 3) it is evident that runoff and chemical transport in runoff began much earlier. Summation of the pesticide mass loss (%) from 0 to 150 min, 0 to 72 min, and 73 to 150 min provides the measured runoff loss, predicted infiltration loss, and predicted runoff loss, respectively. Subtraction of the predicted runoff loss from the measured runoff loss results in the under prediction of pesticide mass loss with runoff when infiltration is presumed to be chronologically separated from runoff. The error in this assumption explains a large amount of the observed under prediction from TurfPQ for dicamba, flutolanil and chlorpyrifos (Table 2). Observations for 2,4-D and MCPP in this example require additional investigation. Changing the chronological separation of infiltration and runoff and replacing daily (24 h) precipitation inputs with more frequent time steps should allow the model to more accurately predict intense storm events.

Sensitivity Analysis of Organic Carbon Partition Coefficient at Three Organic Carbon Levels

Sensitivity analysis evaluates the effect of input errors on computed model outputs by varying a single parameter while holding other parameters constant (McCuen, 2003). Changes in the results due to the changes in a single parameter may then be plotted to gain an understanding of the sensitivity of the parameter. For the TurfPQ model, sensitivity analysis of the K_{OC} parameter was performed for a theoretical runoff event. In this test, the application rate was set at 500 g ha^{-1}, the CN was 57 and the rainfall (same day) was 70 mm for presaturated soil (11 mm of rain each of the previous 5 d). This scenario produced 23.0 mm of runoff according to the CN method. The half-life was set to 5 d. Organic carbon partition coefficient values were chosen to include and span the values of the five pesticides in this study. The K_{OC} range was set to 0, 5, 10, 13, 20, 25, 48, 100, 150, 500, 800, 1000, 3000, 5000, 7000, 9930, 11,000, and 15,000 L kg^{-1}.

Results of the analysis are plotted in Fig. 4. These trends for low (3000 kg ha^{-1}), mid (10,000 kg ha^{-1}), and high (38,000 kg ha^{-1}) OC contents reflect approximately 0.8, 7, and 32 mm of thatch thickness, respectively, based on the computation of OC in Haith (2001). These values encompass a very wide range, therefore most fairway turf systems would be represented in Fig. 4. As mentioned in the methods section, our turf plots contained a very thick thatch layer, but predicted hydrology matched field results better when the OC content of a moderate thatch layer (10,235 kg ha^{-1}) was used. In terms of Fig. 4, it is likely that our plots are represented by a range between the mid-level and high-level OC trends.

When considering the full K_{OC} range (0–15,000 L kg^{-1}) each trend has a single peak maximum at a specific K_{OC} value. The location of this peak varies for the three OC trends plotted, but the pattern is the same. The K_{OC} values to the left of the peak (lower values) produce lower pesticide mass loss because most of the pesticide is leached due to infiltration and less is available for runoff. Values to the right of the peak start to produce decreasing mass loss because the higher K_{OC} results in greater adsorption to turf and less dissolution into runoff.

The left half of Fig. 4 (K_{OC} = 0–160 L kg^{-1}) is applicable to dicamba, 2,4-D, and MCPP (K_{OC} = 13–20 L kg^{-1}). In this plot, the maximum mass loss never exceeds 20% for any combination of K_{OC} and OC tested. As several of our measured mass losses exceeded 20%, particularly for dicamba, the TurfPQ prediction error does not seem to be attributable to merely parameter estimation. Even if the K_{OC} and OC were accurately known, the model predictions would still be limited to a 20% mass loss with runoff. Flutolanil and chlorpyrifos are applicable to right half of Fig. 4 (K_{OC} = 500–15,500 L kg^{-1}). In this plot, the trends for mid-level OC content produce losses of 2.6% for K_{OC} = 800 L kg^{-1} (flutolanil) and 0.2% for K_{OC} = 9930 L kg^{-1} (chlorpyrifos). For both pesticides, these predictions are an underestimation of the mean measured mass loss of this study (5.8% for flutolanil and 0.8% for chlorpyrifos). For a high-level OC content, the underestimation is even more dramatic. From the plot, it can be seen that reasonable errors in the K_{OC} or OC would still likely produce predictions for turf of mid-high thatch levels that are below our measured values. For all five pesticides, errors in parameter estimation of K_{OC} or OC do not appear to be the main cause of the TurfPQ prediction error.

In terms of sensitivity, regions of the plot where the slopes are steep would mean that errors in the K_{OC} would have a greater effect on outcomes. According to Fig. 4 if a pesticide with K_{OC} = 20 L kg^{-1} is mischaracterized as having K_{OC} = 13 L kg^{-1}, the TurfPQ output would change from 16.0% to13.9% for OC = 10,000 kg ha^{-1}. At higher K_{OC} values, the sensitivity is lower; for example, changing the K_{OC} from 9930 to 11,000 L kg^{-1}would cause the mass loss to change from 0.24 to 0.20%. Sensitivity of the OC parameter can also be visualized from the plot, although not via a slope. Vertical jumps from one trend to another provide clues to the sensitivity of OC; the jumps between the three trends vary for different regions of the plot. For a pesticide with a K_{OC} of 10 L kg^{-1}, the computed mass loss would be 5.3, 12.2, 16.8% for OC = 3000, 10,000, and 38,000 kg ha^{-1}, respectively. Therefore, it is important to have an accurate idea of the organic carbon content or the results can vary widely. Even for a lower mobility pesticide, such as flutolanil (K_{OC} = 800 L kg^{-1}), the computed losses were 0.6, 2.6, and 7.3% for low, mid, and high OC values; this spread of outcomes is quite high.

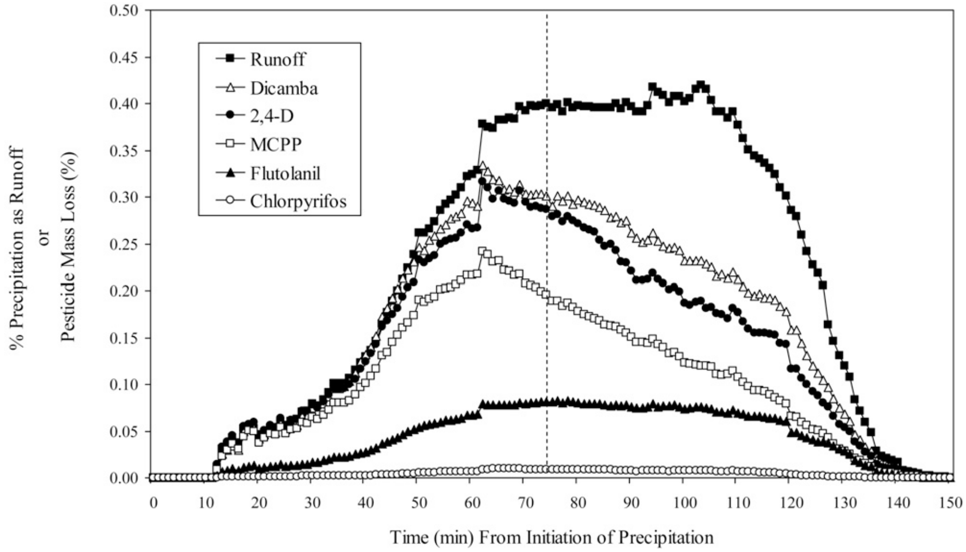

Fig. 3. Hydrograph and chemographs representing the average of the 13 runoff events. Runoff quantities are reported as a percentage of total simulated precipitation. Pesticide mass loss in runoff is reported as the percentage of applied active ingredient. The vertical broken line depicts the timing of the completion of infiltration and the initiation of runoff based on the model's assumption of chronologically separated infiltration and runoff.

Table 2. Effect of infiltration error on the under prediction of pesticide mass loss (%) with runoff.

	Mass loss (%) of pesticides in runoff				
Parameter	**Dicamba**	**2,4-D**	**MCPP**	**Flutolanil**	**Chloropyrifos**
Chemograph data (Fig. 3)					
Measured runoff loss (0–150 min)	23.09	20.55	14.59	6.37	0.62
Predicted infiltration loss (0–72 min)†	10.13	9.64	7.59	2.36	0.25
Predicted runoff loss (73–150 min)†	13.20	11.15	7.16	4.05	0.37
Under prediction‡	9.89	9.40	7.43	2.32	0.25
Measured and predicted data (Fig. 2A-E)					
Measured runoff loss	24.60	20.70	14.90	5.90	0.80
TurfPQ predicted runoff loss	13.70	15.60	15.50	2.50	0.20
Under prediction‡	10.90	5.10	−0.60	3.40	0.60

† Assumes chronological separation of infiltration and runoff.

‡ Under prediction = measured runoff- predicted runoff.

Sensitivity Analysis of Pesticide Half-Life

Sensitivity analysis of the pesticide half-life was performed for a theoretical runoff event holding the CN at 57 and OC at 10,235 g ha^{-1}, while changing the half-life from 0.1 to 500 d. Two sets of analyses were run, one representing a high mobility pesticide (dicamba, K_{OC} = 13 L kg^{-1}) and the other representing a low mobility pesticide (flutolanil, K_{OC} = 800 L kg^{-1}). For both analyses varying the pesticide half-life did not change the predicted mass of pesticide in the runoff. Therefore the under prediction of pesticides loss with runoff in the TurfPQ outputs compared to the measured loss was not the result of error in the half-life parameter.

Sensitivity Analysis of Curve Number

As a final study, alterations of the CN were performed to gauge the sensitivity of this parameter. Curve number was able to be calibrated in this study; however, it would not be practical to measure the hydrology of every turf system. Published values may be reasonable estimates, but it is expected that errors in runoff quantity would exist if CN was selected from a literature value. For this analysis, CN adjustment was performed for a theoretical event involving dicamba. Having the lowest K_{OC} value in the study, this pesticide was expected to be most sensitive to runoff quantity. Rainfall was set to 70.0 mm with presaturation (11 mm of rain each of the previous 5 d), the OC was held at 10,235 kg ha^{-1}, and the mean application rate (237.41 g ha^{-1}) was used. Figure 5 shows the results of CN adjustment ± 10 increments from 57. Two different quantities are shown together on the same plot, runoff quantity as a percentage of precipitation and dicamba mass loss in runoff as a percentage of applied active ingredient. The symbols at CN = 57 are filled solid for reference. For the lowest and highest CNs tested, 47 and 67, the percentage of precipitation is 9.8 and 19.0%, producing dicamba losses of 19.7 and 47.4%, respectively. The plot indicates that errors in CN can be tolerated perhaps plus or minus a few integers. More severe errors in CN could start to seriously affect runoff quantity (and in turn, pesticide mass loss).

Model Efficiency

Figure 6 shows the measured pesticide mass loss (as a percentage of applied) vs. predicted mass loss for all data tested in

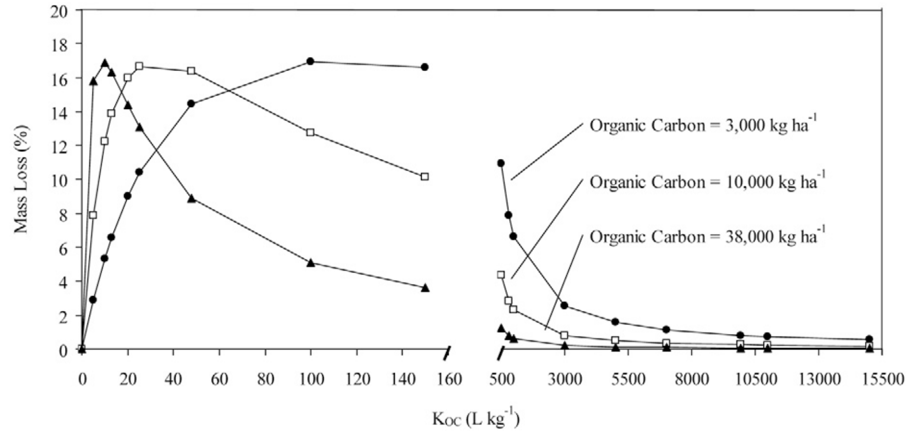

Fig. 4. Sensitivity analysis evaluating the effect of pesticide (soil organic carbon partition coefficient, K_{OC}) and turf (organic carbon in turf vegetation, OC) input parameters on TurfPQ predicted mass loss of pesticides in runoff.

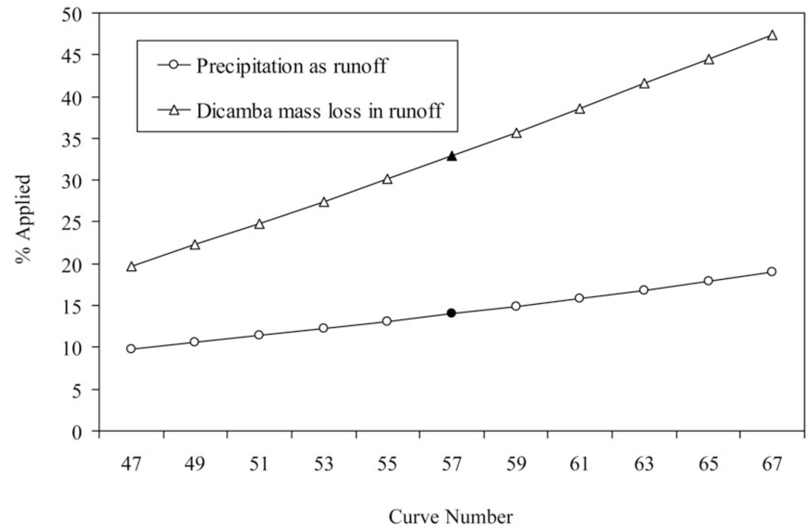

Fig. 5. Sensitivity analysis evaluating the effect of the curve number on TurfPQ predicted runoff and dicamba mass loss in runoff. Runoff quantities are reported as a percentage of total simulated precipitation. Dicamba mass loss in runoff is reported as the percentage of applied active ingredient.

the TurfPQ_MH model. The fine dotted trend line is a unity line, designating perfect correlation. The fact that most of the data is below this line indicates the overall under predictions produced by the model. Closer observation of Fig. 6 reveals dicamba, a high mobility pesticide, was under predicted almost as frequently as the low mobility pesticides, flutolanil and chlorpyrifos. We speculate this is the influence of the predicted infiltration error as described previously (Fig. 3, Table 2). Dicamba has the lowest Koc of the five evaluated pesticides and the largest application rate of the three more mobile pesticides (Table 1). Therefore we would expect dicamba to be the most readily transported with water. The hydrograph and chemographs in Fig. 3 show the transport characteristics of the five pesticides with runoff. Interestingly, the number of under predictions of the three high mobility pesticides (dicamba, 2,4-D, and MCPP) corresponds with the chemographs where dicamba had the greatest mass loss and the most under predictions (10 of 13) followed by 2,4-D (9 of 13 under predictions) and MCPP (3 of 13 under predictions).

The thick solid line in Fig. 6 shows the correlation of the plotted data, yielding r = 0.64. The Nash-Sutcliffe efficiency (Nash and Sutcliffe, 1970) was computed as E = 0.48. With the TurfPQ_CN model, the r was 0.56 and the efficiency was 0.41. The efficiency values would ideally be higher, but are respectable outcomes considering the relative simplicity of the model and the low number of data points evaluated. Similar values for r and model efficiency were reported by Haith (2001).

Conclusions

The TurfPQ model was tested for runoff simulations from turf managed as a golf course fairway. The model predicted runoff quantities fairly well using the curve number method. Predictions of MCPP were close with several overpredictions observed for MCPP and 2,4-D. Predictions of dicamba, flutolanil, and chlorpyrifos were consistently underestimated. In some instances, dicamba was severely under predicted. Sensitivity analyses indicated that errors in OC or K_{OC} estimations may contribute but were not the main cause of underpredictions. The greatest

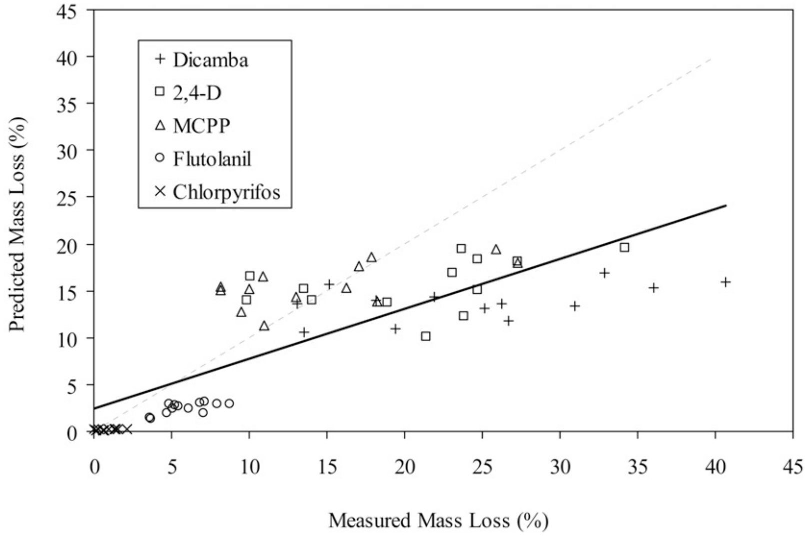

Fig. 6. Correlation plot of measured mass loss versus predicted mass loss using measured hydrology for all runoff events and pesticides included in the study. The broken trend line is a unity line, designating perfect correlation. Pesticide mass loss is reported as a percentage of the applied active ingredients.

source of error was in the timing of predicted infiltration and runoff, which influenced the predicted availability of pesticides for transport with runoff. Changing the chronological separation of infiltration and runoff and replacing daily (24 h) precipitation inputs with more frequent time steps should allow the model to more accurately predict larger intense storm events as evaluated here. Additional research to obtain OC estimations based on larger data sets and turf vegetation K_{OC} should also improve predictions. For this study, the systematic under predictions were of concern, but the model has been shown to produce conservative overestimations for other data sets (Haith, 2001). The advantages of the model in its simplicity, low data requirements, and ease of use are strong arguments for its consideration as a general-use chemical transport model for turf. However, it is recommended to investigate this model with more extensive data sets which include runoff scenarios of a wider scope to anticipate when overpredictions or underpredictions will occur.

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